

AD-A062 619 GENERAL ELECTRIC CORPORATE RESEARCH AND DEVELOPMENT --ETC F/G 7/3
SOLID STATE MATERIALS DERIVED FROM PLANAR METAL COMPLEXES. (U)
DEC 78 L V INTERRANTE, J S KASPER F44620-76-C-0006

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SOLID STATE MATERIALS DERIVED
FROM PLANAR METAL COMPLEXES

DEC 11 1978

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ADA062619

FINAL SCIENTIFIC REPORT

Period Covered: 1 July 1977 through 30 September 1978

Prepared for

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH

DIRECTORATE OF CHEMICAL SCIENCES
BOLLING AIR FORCE BASE, BLDG. 410
Washington, DC 20332

DDC

PROPRIETARY

DEC 26 1978

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Contract No. F44620-76-C-0006

December 1978

General Electric Company
Corporate Research and Development
Schenectady, New York 12301

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH (AFSC)
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20. ABSTRACT

property measurement techniques. In addition, the crystal structures have been characterized using single crystal x-ray diffraction methods. The results have been used to obtain information regarding the electronic and magnetic interactions occurring in the solid state and to derive synthetically useful structure-property relationships. ↙

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FOREWARD

This report describes work carried out over the period 1 July 1975 to 30 September 1978 on the Contract "Solid State Materials Derived from Planar Metal Complexes". The principal focus of this work has been on the preparation and study of π -donor-acceptor compounds derived from the interaction of the organic donors, tetrathiafulvalene and tetra-thiotetracene, with bis(1,2-ethylenedithiolene) metal complexes as the π -acceptors. These new compounds have been studied using electrical conductivity, magnetic susceptibility, and various other types of solid state property measurement techniques. In addition, the crystal structures have been characterized using single crystal x-ray diffraction methods. The results have been used to obtain information regarding the electronic and magnetic interactions occurring in the solid state and to derive synthetically useful structure-property relationships.

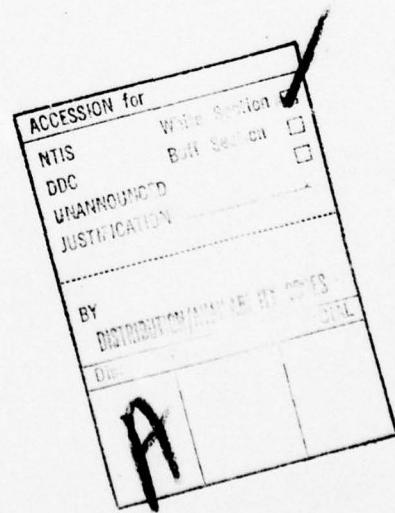


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SECTION I

INTRODUCTION

Work on the research program "Solid State Materials Derived from Planar Metal Complexes" was begun on July 1, 1975 with the following basic objectives:

- o To prepare new organic-transition metal complex materials with scientifically interesting and technologically useful solid state properties.
- o To develop structure-property generalizations useful in the design of molecular systems to achieve desired specific solid state property objectives.

The research was approached from the following perspective: first, specific metal complex systems were selected for use in the efforts to synthesize new materials. The selection was based on criteria such as the overall planarity of the metal complex unit (desirable from the viewpoint of promoting one-dimensional (1-D) stacking interactions), its capacity to undergo reversible redox behavior, its ability to yield species with unpaired electrons in orbitals of π -symmetry, and its structural flexibility, i.e., its capacity for systematic alteration of structural parameters such as the metal atom and ligand substituents, within the context of a common basic molecular framework. The latter criterion was viewed as particularly important in order to provide the structural variability needed for the exploration of molecular structure-solid state property relationships and as a framework to help guide the course of our synthesis efforts.

These metal complex systems were then used, usually in combination with various organic molecules, for the preparation of new π -donor-acceptor compounds and in efforts to prepare "mixed valence state systems" formally derived from combinations of two or more redox forms of the same molecular unit. The new compounds so prepared were characterized as to molecular composition, screened for interesting or unusual solid state electrical and magnetic properties and, where appropriate, studied in detail in the form of single crystals. Detailed structural studies on selected materials were also undertaken as justified from the viewpoint of interesting solid state behavior and to obtain information regarding molecular packing and separations.

The metal complex system chosen as the initial and principal focus of our synthesis efforts was the bis(1,2-ethylenedithiolene) (BDT) metal complex system, illustrated in Figure 1. In addition to satisfying all of the necessary criteria, this system had been

shown in our previous preliminary studies to yield new solid state materials with interesting behavior in combination with the organic π -donor, tetrathiafulvalene (TTF) (Ref. 1). In addition to more fully exploring the range of structural parameters available in this metal complex system and its π -D·A combinations with other organic π -donors, we have also examined various other metal complex systems, including the bis(1,2-benzenedithiolene metal complexes and $\text{NiS}_4\text{N}_4\text{H}_2$, as potential alternatives to the bis(1,2-ethylenedithiolene) complexes as π -acceptors, as π -donors toward the bis-dithiolene complexes and organic π -acceptors and as possible 1-D mixed valence state systems. Finally, the organic compound bithiazole (BTA) has been studied in a preliminary way as a potential source of bi-nuclear metal complexes and as a possible solid state analog of TTF.

The results of these studies are summarized in the next section according to the different types of materials investigated.

SECTION 2

SUMMARY OF PROGRESS

I. π-DONOR-ACCEPTOR (π-D·A) COMPOUNDS DERIVED FROM PLANAR METAL COMPLEXES

A. Tetrathiafulvalene (TTF)-Metal Bis-dithiolene (MBDT) Donor-Acceptor Compounds

A systematic study of the TTF-MBDT system was undertaken prior to the beginning of this contract, leading to several π -D·A compounds with novel solid state properties (Ref. 1). During the present contract period this work has been extended considerably, yielding both new compounds and an improved understanding of their physical behavior. Much of this work has been carried out in our own laboratories; however, we have also been aided considerably in these efforts by scientists from other institutions who were able to provide special equipment and/or expertise which were not available in our laboratories.

A more detailed description of the structural work carried out on these systems is given elsewhere in this report (see part III). The focus of this portion is on the synthesis and physical property studies.

The TTF- $\text{MS}_4\text{C}_4\text{H}_4$ System

The electrochemical reduction potentials for the neutral $\text{MS}_4\text{C}_4\text{H}_4$ ($M = \text{M, Pd, Pt}$) complexes are approximately the same as that for the organic compound, tetracyanoquinodimethane (TCNQ), suggesting the possibility of comparable π -acceptor characteristics (Ref. 2). This observation, along with the other gross similarities in molecular and electronic structure exhibited by these compounds, provides a basis for special interest in π -D·A compounds formed by the interaction of the $\text{MS}_4\text{C}_4\text{H}_4$ complexes with organic π -donors such as tetrathiafulvalene (TTF) and tetrathiotetracene (TTT) (Figure 1). Although these efforts have not produced any close relatives of TTF-TCNQ in terms of either structure or conductivity, the new compounds obtained have turned out to be of considerable interest in their own right and their study has provided some new insights into the chemistry and physics of π -D·A compounds.

Our prior work on the TTF- $\text{MS}_4\text{C}_4\text{H}_4$ system produced two new π -D·A compounds, the $\text{TTF}_2\text{NiS}_4\text{C}_4\text{H}_4$ derivative and a material of approximate composition, $2\text{TTF} \cdot 3\text{NiS}_4\text{C}_4\text{H}_4$. These compounds were obtained by evaporation and slow cooling of acetonitrile solutions containing different proportions of TTF and $\text{NiS}_4\text{C}_4\text{H}_4$.

Work carried out during the present contract period on these compounds has included the completion of conductivity measurements as a function of crystallographic direction on the $\text{TTF}_2\text{NiS}_4\text{C}_4\text{H}_4$ compound, the structural characterization and detailed conductivity study of the $2\text{TTF}\cdot 3\text{NiS}_4\text{C}_4\text{H}_4$ derivative and efforts to prepare analogous compounds using the $M = \text{Pt, Pd, Au and Cu}$, $\text{MS}_4\text{C}_4\text{H}_4^{n-}$ ($n=0, 1$) complexes.

The structural studies on these compounds (see part III) along with the conductivity measurements have provided a detailed picture of the relationship between electronic conductivity and the geometrical arrangement and separation of the molecular units in the solid. In the $(\text{TTF})_2\text{MS}_4\text{C}_4\text{H}_4$ compound, where a columnar stacking of the TTF units occurs along the b-axis direction in the crystal, the highest conductivity ($\sim 10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}$) is found along this axis, reflecting, presumably, the appreciable π -orbital overlaps within the TTF stacks. Consistent with the conclusion that the odd π -electrons in this system are paired within localized π -molecular orbitals associated with the $(\text{TTF}^+)_2$ units in the structure (Ref. 3), the conductivity is thermally activated with an activation energy of $\sim 0.2\text{V}$. This activation energy is presumably associated, at least in part, with the excitation of these paired π -electrons into conduction band states in the crystal associated with the extended π -orbital overlap along the TTF stacks. Although significantly reduced relative to that along the b-axis, the magnitude of the conductivity along the other two orthogonal directions in the crystal still shows a substantial dependence on direction. Here the conductivity along the c-axis, where additional, more distant TTF molecules are positioned appropriately for significant inter-unit π -orbital interactions, is significantly higher than that in the direction orthogonal to the bc plane.

Another notable feature of the $\text{TTF-NiS}_4\text{C}_4\text{H}_4$ system is the remarkable difference in the D-A charge transfer characteristics of the two compounds obtained. The fact that the $(\text{TTF})_2\text{NiS}_4\text{C}_4\text{H}_4$ compound is charge-transferred, i.e. the actual composition is $\text{TTF}^\circ\text{TTF}^+\text{NiS}_4\text{C}_4\text{H}_4^-$, whereas the compound $(\text{TTF})_2(\text{NiS}_4\text{C}_4\text{H}_4)_3$, which has the same two components in different proportions is not unprecedented among π -D-A compounds and suggests a rather close match of the effective D ionization potential and A electron affinity for this system. In view of the fact that TCNQ forms with TTF a π -D-A compound which is partially charge transferred in the ground state, this observation provides support for the supposition that the $\text{MS}_4\text{C}_4\text{H}_4$ complexes and TCNQ are similar in their π -acceptor characteristics. In the case of TTF-TCNQ however, the result is a two stack, segregated D-A system with a semi-metallic band structure rather than the two semiconducting compounds with differing

stoichiometries and charge transfer characteristics observed for the TTF-NiS₄C₄H₄ system. The difference here may reflect the differing tendencies of the two types of acceptor units to assume a closely stacked structure with a delocalized 1-D electronic configuration. The reason for the apparent reluctance of the NiS₄C₄H₄ system, and possibly the MBDT complexes in general, to form such conductive 1-D stacks remains unclear at present.

The interesting results obtained with the TTF-NiS₄C₄H₄ system encouraged efforts to explore its extension through the use of the related MS₄C₄H₄ (M = Pd, Pt, and Cu) complexes as replacements for NiS₄C₄H₄. Several attempts were made during the course of this contract to obtain such materials, using both direct reaction procedures involving the neutral MS₄C₄H₄ (M = Pd, Pt) complexes and metathesis reactions with the MS₄C₄H₄⁻ and TTF⁺ species. These attempts either led to no reaction or decomposition of the starting materials (CuS₄C₄H₄⁻). In no case was there any indication of π -D·A compound formation. These results can be understood on the basis of the difference in the chemical behavior of these MS₄C₄H₄ⁿ⁻ species. The neutral M = Pd, Pt derivatives are dimerized in the solid state and are poorly soluble in organic solvents. This low solubility apparently prevents formation of a π -D·A compound from solutions of the neutral components. In the case of CuS₄C₄H₄ⁿ⁻ the instability of the neutral form of this compound leads to decomposition on mixing of TTF⁺ and CuS₄C₄H₄⁻.

TTF·MS₄C₄(CF₃)₄

The use of the highly electropositive MS₄C₄(CF₃)₄ complexes as π -acceptors in combination with TTF as the π -donor leads to a series of 1:1 π -D·A compounds which are fully charge transferred in the ground state and thus exist in solution and in solid state as the TTF⁺MS₄C₄(CF₃)₄⁻ species. These compounds crystallize in structures which are comprised of alternate D⁺A⁻ stacks and exhibit exceptionally low solid state conductivities. Despite these low conductivities they have turned out to be among the most interesting and important π -D·A compounds known due to their remarkable magnetic properties and attendant structural transformations. These features have been explored in detail during the current contract period, both in our laboratory and elsewhere in collaborative research efforts with scientists from other institutions.

As a result of these studies, a much improved understanding of the solid state magnetic interactions and the effects of these interactions on the structure and properties has been obtained. This new information is likely to be of considerable long-term interest both to solid state theorists and experimentalists interested in the physics of low dimensional systems.

In the case of $\text{TTF}\cdot\text{NiS}_4\text{C}_4(\text{CF}_3)_4$, which is structurally distinct from the other members of the $\text{TTF}\cdot\text{MS}_4\text{C}_4(\text{CF}_3)_4$ series of compounds, evidence has been obtained for a metamagnetic transition in the vicinity of 4°C , whose occurrence is apparently highly dependent on the purity and/or the degree of crystal perfection of the sample, (Ref. 4). The observation of such a transition in organic or metallo-organic systems is a rare occurrence and is quite notable from this standpoint alone. In certain samples this transition is apparently suppressed, presumably by impurities and/or crystal defects, leading to ferromagnetic-like behavior which persists down to the lowest temperatures investigated ($\sim 1^\circ\text{K}$).

Using a vapor phase preparation procedure, followed by recrystallization from purified acetonitrile, we were able to produce samples which gave a clean metamagnetic transition at $\sim 4^\circ\text{K}$ thus revealing the unusual sensitivity of this system to subtle differences in composition and/or defect concentration.

The origin of these sample dependent effects and the detailed nature of the magnetic exchange system which leads to the observed properties remain to be determined; however, at least qualitatively it is possible to account for the apparent existence of at least 3 different magnetic exchange interactions (2 antiferro- and 1 ferromagnetic) on the basis of the crystal structure. Figure 2 shows a portion of the $\text{TTF}\cdot\text{NiS}_4\text{C}_4(\text{CF}_3)_4$ structure viewed perpendicular to the (100) plane in which two types of exchange interactions can be envisioned. If we add to this picture a third, yet weaker, exchange interaction of antiferromagnetic character between these sheets of molecules, it is possible to account qualitatively for all of the various changes in susceptibility with temperature as well as the magnitude of the saturation magnetization at low temperatures ($4 \rightarrow 40\text{K}$), which suggests that only $\sim 1/3$ of the available spins of the molecular units are effectively contributing to the ferromagnetic exchange observed in this region.

Further work on this system is needed to provide a detailed test of this exchange model. However, it is interesting that the same basic features of this model (i.e., ferromagnetic exchange within the alternate D^+A^- stacks and

antiferromagnetic exchange between nearest neighbor units in adjacent D^+A^- stacks) can be applied to the other compounds of the $TTF \cdot MS_4C_4(CF_3)_4$ series with relatively minor modification. Thus the $TTF \cdot PtS_4C_4(CF_3)_4$ compound, which exhibits dominant ferromagnetic coupling at higher temperatures and then orders antiferromagnetically at low temperatures, (Figure 3), differs only in the relative magnitude of these exchange interactions, with the intrachain ferromagnetic coupling apparently the dominant feature. The reason for this change in the hierarchy of exchange interactions can be understood on the basis of the crystal structures which, although closely similar in many respects, differ substantially in the relative approach of the D^+ and A^- units between the $D^+ \cdot A^-$ stacks (Ref. 4). In the $TTF \cdot NiS_4C_4(CF_3)_4$ structure, inter-chain $D \cdot A$ contact is facilitated leading, presumably, to a dominant antiferromagnetic exchange in this case.

During the current contract period the $M = Pt$ compound has been examined in detail, using both magnetic susceptibility studies on a large single crystal and, in collaboration with Dr. T. Wei of the University of Pennsylvania, specific heat measurements (Ref. 5). These studies, which are reported in a recent publication, show that an appreciable anisotropy in χ develops below $\sim 12K$ leading to a strong drop in χ_b (Fig. 3). A broad anomaly in the specific heat appears between 5K and 9K. These effects indicate the onset of antiferromagnetic ordering in this system below $\sim 8K$, arising presumably from the antiferromagnetic coupling between the 1-D ferromagnetic $D^+ \cdot A^-$ chains.

In this case neither the temperature of the "transition" to an AF state nor the sharpness of the transition seemed to be much affected as a result of efforts to obtain a purer sample by vapor phase synthesis followed by repeated recrystallizations from acetonitrile. Attempts to deliberately dope the compound with the diamagnetic $AuS_4C_4(CF_3)_4$ ion did produce an observable decrease in the transition temperature, but only at relatively high levels of dopant ($\sim 10\%$).

The $TTF \cdot MS_4C_4(CF_3)_4$ $M = Cu$ and Au compounds, although isostructural with the $M = Pt$ derivative, exhibit quite different magnetic properties. The magnetic susceptibility between 12 and 200K is modeled quite accurately by a system of $S = 1/2$, AF Heisenberg chains of spins with a single J_{AF}/k of 77K for $M = Cu$ and 68K for $M = Au$. The susceptibility is isotropic at all temperatures. Below 12K for Cu and 2.1K for Au, the susceptibility decreases sharply toward zero, independent of the orientation of the crystals in the applied field (Fig. 3). These data display with classic simplicity the behavior expected for a "spin-Peierls" transition, i.e., a progressive spin-lattice dimerization occurring below a transition temperature in a system of AF Heisenberg chains.

In the past three years of AFOSR contract supported work these compounds have been studied in considerable detail in several different laboratories leading to a much more complete characterization of their unusual properties and a better understanding of the origin of this behavior. In collaborative work with scientists at Bell Labs and MIT, the structural consequences of the spin-Peierls transition have been explored using both x-ray and neutron scattering methods. The occurrence of a progressive lattice dimerization as anticipated for a spin-Peierls transition below 12K in the M=Cu derivative was verified and the order parameter was shown to be consistent with expectations based on the mean-field spin-Peierls theory of Pytte. The direction of dimerization was shown to be not along the D^+A^- stacking direction (c_F) as had been previously anticipated but instead along either the a_p or c_p primitive cell directions which represent the directions of closest approach of the TTF^+ units in the structure (Ref. 6).

An analysis of the intensities of the superlattice reflections observed at 4K for the M=Cu system has recently been completed which shows that it is, in fact the c_p direction along which dimerization occurs (Fig. 4), indicating that this is the principal exchange direction in the solid. The results of this study are outlined in more detail in the structural section of this report.

The choice of the c_p axis as the principal exchange direction may be understood in view of the change in the crystal structure of the $TTF \cdot CuS_4C_4(CF_3)_4$ compound which occurs at $\sim 250^\circ K$. A detailed crystallographic analysis by x-rays of the structures of this compound above and below the first order phase transition at this temperature has been carried out by Drs. Delker and Stucky of the University of Illinois on our samples which shows marked changes in certain lattice parameters (Ref. 7). In particular the c_p and a_p dimensions, which are only slightly different in the room temperature structure, became much different in the low temperature phase with $c_p \sim 1.8\text{\AA}$ shorter than a_p (Fig. 4). The driving force for this transition, which preserves the basic symmetry of the unit cell, is apparently the ordering of the CF_3 groups, which are rotationally disordered in the room temperature structure, along with an attendant decrease in the volume of the cell.

The conclusion that the c_p axis is coincident with the principal exchange direction in the solid and the inference that direct exchange between the TTF^+ units along this direction is occurring is supported by the results of susceptibility measurements carried out on a close relative of $TTF \cdot CuS_4C_4(CF_3)_4$ recently prepared in our laboratory. Using a sample of $n\text{-}Bu_4N^+CuSe_4C_4(CF_3)_4$ obtained from Professor B. Hoffman of Northwestern University we have succeeded in preparing a $TTF \cdot CuSe_4C_4(CF_3)_4$ compound which is closely similar to its all-sulfur relative both structurally and chemically.

This compound was prepared by a methathesis procedure, using TTF⁺ and the CuSe₄C₄(CF₃)₄ salt, analogous to that used for the CuS₄C₄(CF₃)₄ derivative. X-ray powder patterns and single crystal precession measurements show that its crystal structure at room temperature is virtually identical to that of the sulfur analog with the differences in unit cell parameters lying within the error limits of the precession measurements. Static susceptibility measurements show the occurrence of a clean first order phase transition in the same temperature regime as that of the S analog. The overall χ vs. T behavior below the first order transition is also closely similar to that observed for the S compound with the maximum in χ vs. T occurring at virtually the same temperature. Since the position of this maximum in χ is directly determined by the magnitude of the exchange coupling constant, J_{AF} , this indicates that the exchange interaction is essentially unchanged by this chemical substitution. This provides good evidence for the assumption of a direct TTF⁺ exchange process in the TTF·CuS₄C₄(CF₃)₄ system with the CuS₄C₄(CF₃)₄ anions not participating significantly in the magnetic coupling.

The participation of these ions in the lattice dimerization which occurs below 12K in this system is indicated by the χ vs. T data below 12K which show a depression in the transition temperature to 6°K for the Se system. The observation from the structural study at 4°K that the CuS₄C₄(CF₃)₄⁻ ions do in fact move in this transition is consistent with this conclusion (see part III).

Attempts to extend this exploration of the effects of chemical modifications in the TTF·CuS₄C₄(CF₃)₄ structure on the magnetic properties to the preparation of an analogous TSeF·CuS₄C₄(CF₃)₄ compound have been unsuccessful thus far. Oxidation of TSeF with chlorine in carbon tetrachloride gave a material presumed to be TSeCl; however a solution of this in methanol when combined with a methanolic n-Bu₄N⁺CuS₄C₄(CF₃)₄⁻ solution yielded only a small amount of material which, although not fully characterized, is clearly not the desired isostructural TSeF derivative. Other methods for generating TSeF⁺ in the presence of the CuS₄C₄(CF₃)₄⁻ ion (both chemical and electrochemical) were also tried but failed to yield the desired product.

Replacement of the Cu in TTF·CuS₄C₄(CF₃)₄ by Au leads to a compound which is analogous in many respects with the Cu derivative but which also shows some important differences. The structural changes in this case as a result of the first order transition at ~200°K and the spin-Peierls transition at 2.1K have not been fully characterized; however, it appears from preliminary work that basically the same structural changes occur here with possibly a larger change in unit cell

dimensions at 200°K. Specific heat measurements on this compound suggest less satisfactory agreement with a purely mean-field description for the spin-Peierls transition than is the case for the Cu derivative, possibly due to a greater importance of 1-D magnetic fluctuations in the Au case (Ref. 8).

The effect of magnetic field on the spin-Peierls transition has also been studied in the case of the M=Cu compound using both neutron scattering techniques and susceptibility measurement methods. The magnetization studies were carried out on a polycrystalline sample of this compound at the high field magnet facility at the CNRS Laboratoire Louis Néel in Grenoble, France by D. Bloch (Ref. 9). Inflections in the magnetization (M) vs. applied field (H) and M vs. temperature (T) curves were used to derive an H vs. T_{s-p} curve which is illustrated in Figure 5. These data imply a general depression of the transition temperature with field with apparent complete suppression above ~120 K0e. More work is needed before any detailed conclusions can be drawn; however, the observed lowering of the transition temperature constitutes strong confirmatory evidence for the magnetic origin of the transition and also argues against a conventional magnetic ordering transition.

The neutron scattering studies were done in collaboration with D. Moncton of Bell Laboratories at the Brookhaven National Laboratories and consisted of elastic scattering measurements of certain Bragg reflections characteristic of the dimerized structure as a function of temperature and magnetic fields of up to 80 K0e. These measurements indicate a decrease in the spin-Peierls transition temperature with increasing field in accordance with the relation $\Delta T_{s-p} = KH^2$. Such a relation has been predicted theoretically using mean field theory for the spin-Peierls transition and its observation in the case of $TTF \cdot CuS_4C_4(CF_3)_4$ provides further support for the application of the spin-Peierls description to this system (Ref. 10).

Further experiments of these two types are planned in order to more fully characterize the magnetic field effects on the spin-Peierls transition. These further experiments will include a study of the M=Au derivative by neutron scattering methods. This compound, by virtue of its lower transition temperature is expected to show complete suppression of the transition at much lower fields than the Cu derivative, thus permitting a detailed structure evaluation of this system in the regime of low T and high H, where possible changes in the periodicity of the lattice have been anticipated theoretically (Ref. 10a). The preparation of large single crystals of the d-TTF-AuS₄C₄(CF₃)₄ compound in order to check out these predictions and to explore via inelastic neutron scattering the magnetic spin interactions above T_{s-p} is in progress.

Other work carried out on the TTF- $\text{MS}_4\text{C}_4(\text{CF}_3)_4$ ($\text{M} = \text{Cu}, \text{Au}$) system during the current contract period includes a collaborative study of the $\text{M} = \text{Cu}$ system via H^1 nmr measurements, which have characterized the changes in spin-lattice relaxation time, T_1 , with temperature. The results provide support for the supposition of a 1-D, $S = 1/2$ Heisenberg exchange system above $T_{\text{s-p}}$ and show quite clearly the progressive formation of the gap in the magnetic energy spectrum below $T_{\text{s-p}}$ (Ref. 11).

B. Tetrathiotetracene (TTT)-MBDT Donor-Acceptor Compounds

Our study of π -D-A compounds which employ MBDT complexes as the π -acceptors was extended during the current contract period to include tetrathiotetracene (TTT) as the π -donor. Tetrathiotetracene has been used in combination with TCNQ, I_2 and other acceptors to yield a series of conductive π -D-A compounds analogous in many respects to the corresponding TTF derivatives (Ref. 12).

In the case of the MBDT complexes the best results were achieved in the case of the $\text{NiS}_4\text{C}_4\text{H}_4^-$ compound, which yielded a conductive TTT derivative of the type $\text{TTT}_{1.2}\text{NiS}_4\text{C}_4\text{H}_4^-$. This compound was obtained by slow cooling of a solution of a 1:1 molar proportion of TTT and $\text{NiS}_4\text{C}_4\text{H}_4^-$ in hot trichlorobenzene. On slow cooling, reflective, needle-like crystals were obtained, for which the $\text{TTT}_{1.2}\text{NiS}_4\text{C}_4\text{H}_4^-$ empirical formula was ascertained by means of elemental analyses and x-ray structural studies. The x-ray structural study (see part III for details) indicated colinear stacks of TTT^{n+} units separated by sheets of non-stacked $\text{NiS}_4\text{C}_4\text{H}_4^-$ units. The $\text{TTT}_{1.2}\text{NiS}_4\text{C}_4\text{H}_4^-$ empirical formula derives from an exceptionally long repeat distance along the c-axis (43.6 Å) such that 12 TTT^{n+} and 10 $\text{NiS}_4\text{C}_4\text{H}_4^-$ units are contained in the unit cell.

Charge transfer in the ground state to yield TTT^+ and $\text{NiS}_4\text{C}_4\text{H}_4^-$ units was indicated by magnetic susceptibility and epr measurements. The magnetic susceptibility studies indicate Curie-law behavior with a Curie constant consistent with one unpaired spin per $\text{TTT}_{1.2}\text{NiS}_4\text{C}_4\text{H}_4^-$ formula unit. On the basis of epr studies the unpaired spin was shown to reside on the $\text{NiS}_4\text{C}_4\text{H}_4^-$ units. The TTT^+ units required for charge compensation are not evidenced in the magnetic studies, presumably because they are part of a delocalized TTT^{n+} subsystem which is derived from the 2 TTT and 10 TTT^+ units in each unit cell.

Evidence for a delocalized electronic structure for the TTT^{n+} substructure was obtained from conductivity and thermoelectric power measurements, both of which exhibit temperature dependencies suggestive of systems such as $\text{K}_2\text{Pt}(\text{CN})_4\text{Br}_{0.3}\text{H}_2\text{O}$

and NMP-TCNQ for which a "quasi-1-D metal" description has been applied. In the case of $\text{TTT}_{12}\text{NiS}_4\text{C}_4\text{H}_4$ system the "metallic state", signaled by a conductivity which decreases with increasing temperature in the case of the other "1-D metals", is not achieved prior to thermal degradation of the sample, at $\sim 70^\circ\text{C}$. The higher apparent "metal-insulator transition in this case is believed to derive from the coincidence of the structural repeat distance along the $\text{TTT}^{\text{n}+}$ stacking direction with the repeat distance anticipated for the Peierls distortion assuming a $\frac{1}{12}$ filling of the $\text{TTT}^{\text{n}+}$ conduction band. We believe that these results can be generalized to other 1-D conductor systems which share this characteristic of coincident Peierls and structural repeat distances and suggest that this may be the origin of the apparently high metal-insulator transition temperatures (and correspondingly lower room temperature conductivity) observed for the $\text{TTF}_{11}(\text{SeCN})_6$ compound. The results of these studies are reported in several of our recent publications (Refs. 13-15).

Several attempts to extend the range of TTT-MBDT complexes to include other derivatives of the $\text{MS}_4\text{C}_4\text{H}_4$ series were made, including work with the $M = \text{Pt}$, Pd , and Cu derivatives. For $M = \text{Pt}$ and Pd , isostructural $\text{TTT}_{12}\text{MS}_4\text{C}_4\text{H}_4$ compounds were in fact obtained which showed comparable conductivities and other properties in the polycrystalline state; however efforts to obtain single crystals suitable for detailed comparisons were not successful. Attempts were also made to prepare the $M = \text{Cu}$ and Au analogs, which are of particular interest in view of the diamagnetic character of the respective $\text{MS}_4\text{C}_4\text{H}_4^-$ ions; however, in the $M = \text{Cu}$ case no characterizable new products were obtained from metathesis reactions using $\text{CuS}_4\text{C}_4\text{H}_4^-$, and in the $M = \text{Au}$ case efforts to prepare the as yet unreported $\text{AuS}_4\text{C}_4\text{H}_4^-$ species were not successful.

C. Other Efforts to Obtain π -D·A Compounds Using MBDT Complexes as π -Acceptors

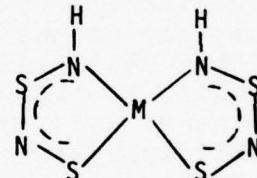
An intensive synthesis effort directed at the preparation of new π -D·A compounds using various MBDT complexes as the π -acceptors was carried out during the current contract period. Several different MBDT complexes of both the 1,2-ethylene-dithiolene and 1,2-arene-dithiolene types (Figure 1) were prepared for use in this study as well as a variety of organic π -donors. Mixtures of the corresponding donors and acceptors, as the neutral D° and A° or the ionic D^+ and A^- species, were co-crystallized from homogeneous solution in various organic solvents and the polycrystalline products studied by means of x-ray powder diffraction and conductivity measurements. The x-ray results were used to distinguish the new compounds from physical admixtures of starting materials and the conductivity measurements to

screen for materials of possible interest as high conductivity molecular solids. The main results are summarized in Table I, which outlines the stoichiometries and powder conductivities of various combinations of the donors and acceptors illustrated in Figure 1.

Those materials with powder conductivities in excess of $\sim 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$ were selected for further study and several attempts to obtain single crystals suitable for more detailed physical measurements were made using both slow cooling crystallization and diffusion techniques. In no case were the desired single crystal samples obtained; instead either microcrystalline materials or various decomposition products invariably resulted.

D. Investigation of the $\text{MS}_4\text{N}_2\text{H}_2$ System as a Source of Potential π -Donors and/or Acceptors

In a search for other planar metal complex systems for use in the formation of novel π -D·A compounds the $\text{MS}_4\text{N}_2\text{H}_2$ system ($M = \text{Ni}, \text{Pt}$) was selected for study. These complexes exhibit an overall planar molecular geometry and a delocalized electronic structure analogous to that of the MBDT complexes. The $M = \text{Ni}$ complex was prepared using literature methods and, as a preliminary to its study in π -D·A systems, its electrochemical behavior was investigated by cyclic voltammetry in collaboration with Dr. G. Farrington of G.E. CR&D. No reversible redox reactions were observed between +2.2 and -1.45v vs. SCE but an irreversible oxidation was noted at +0.96v vs. SCE. An attempt was made to use this compound as a π -donor in combination with the complex $\text{NiS}_4\text{C}_4(\text{CF}_3)_4$ as the π -acceptor; however, the interaction of equimolar amounts of the neutral compounds in this case gave essentially a mechanical mixture of the two components with a very low conductivity.



Efforts to make the corresponding $\text{PtN}_4\text{S}_4\text{H}_2$ complex using a procedure previously reported (Ref. 16) have not been successful. Recently a new preparation of this compound has appeared in the literature offering more promise for its successful preparation (Ref. 17). The study of this compound and the corresponding $\text{MS}_4\text{N}_4(\text{CH}_3)_2$ complexes as potential π -donors and as partially oxidized iodide derivatives constitute worthwhile extensions of our preliminary efforts in this area and will hopefully be carried out during the coming year.

II. STUDIES OF OTHER METAL COMPLEX CONTAINING SYSTEMS

A. One Dimensional Halide-Bridged Mixed Valence Complexes. High Pressure Studies

Over the past six years a number of 1-D metal complex systems have been studied under high pressures in our laboratory in order to investigate crystal structure—solid state conductivity relationships (Refs. 18-20). During the current contract period, prior work on the $\text{Pd}(\text{NH}_3)_2\text{Br}_3$ and $\text{Au}(\text{DBS})\text{X}_2$ (DBS = dibenzylsulfide, X = Cl, Br) complexes was finished up and published (Ref. 21), providing useful information regarding the prospect of observing a Class II+III mixed valence conversion under pressure in this type of 1-D system.

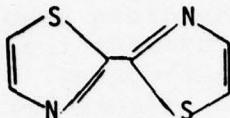
Recently this work has been extended to the structurally related $\text{Pt}(\text{dapn})_2\text{X}(\text{ClO}_4)_2$ and $\text{Pt}(\text{en})_2\text{X}(\text{ClO}_4)_2$ (dapn = 1,2-diaminopropane, en = ethylenediamine, and X = Br, I) compounds which were provided to us by Professor H.J. Keller of Heidelberg University in Germany. The dapn derivatives were of particular interest in view of the initially more nearly equivalent intrachain Pt-X separations in this case as compared to the en and NH_3 derivatives (Ref. 22), providing hope that this system might be more likely to undergo a Class II → III mixed valence conversion. Unfortunately, the Br and I derivatives, as well as the related $\text{Pt}(\text{dapn})_2\text{Br}_3$ compound, remained essentially nonconducting up to the highest pressures investigated (~300 Kbar), preventing even a qualitative comparison of the pressure-conductivity effects in this system.

The only compound of this group which did yield an observable increase in conductivity with pressure was the $\text{Pt}(\text{en})_2\text{I}(\text{ClO}_4)_2$ complex which exhibited behavior much like that previously observed for the other $\text{M}(\text{A})_n\text{X}_3$ type compounds (Ref. 21). Thus the conductivity initially rose rapidly with pressure, peaking near 160Kbar at $\sim 10^{-2}\text{ohm}^{-1}\text{cm}^{-1}$. A gradual decrease in conductivity with increasing pressure was observed beyond 160Kbar.

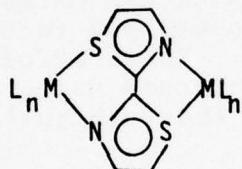
This work effectively extends the group of 1-D mixed-valence systems studied to yet another type of molecular unit and reinforces our previous conclusions regarding the prospect of observing a Class II + III interconversion in such materials. Efforts to measure the conductivity of these new complexes at ambient pressures in the form of both polycrystalline and single crystal samples led only to the conclusion that they are all excellent insulators under these conditions.

B. Studies of Bithiazole (BTS) as a Ligand in Bridged Binuclear Metal Complex Systems and as an Analog of TTF⁺

The compound, bithiazole (BTA), was investigated



as a potential source of novel conductors materials from two quite different viewpoints. First of all, it was recognized that the -1 anion of BTA is isoelectronic with TTF⁺ and that it might, therefore, form structures containing spin-paired, dimeric and/or delocalized, one-dimensionally stacked units analogous to those previously found in the case of TTF⁺. Secondly, the prospect of using this compound as a bridged ligand to form binuclear complexes of the type,



was anticipated from prior work on related tetradentate binucleating ligands such as biimidazole and bipyrimidine (Ref. 23). Such binuclear complexes have been the object of much attention recently, in part from the standpoint of their potential utility as catalysts. Such systems also have been suggested for use as stacked 1-D conductor systems.

In order to investigate these possibilities we undertook the preparation of bithiazole and have carried out some preliminary studies of its redox and ligating characteristics. We developed an improved procedure for its synthesis based on an earlier literature method (Ref. 24) and characterized it using elemental analysis, mass spectral data as well as both C¹³ and H¹ nmr data.

Studies of its redox behavior were undertaken in collaboration with Dr. W. Geiger of the University of Vermont using cyclic voltammetry and it was found to undergo a reversible reduction in acetonitrile solution at -1.90v vs. SCE. We have also found that it can be reduced chemically with alkali metals in aliphatic ether solvents to yield a highly colored and reasonably stable

radical anion in solution (in the absence of air and moisture). This anion has been isolated as its K^+ salt which was found to exhibit thermally activated conductivity behavior (as a pressed pellet) with $\sigma_{25^\circ} \approx 7.5 \times 10^{-5}$ ohm $^{-1}$ cm $^{-1}$. This salt decomposed in air to yield neutral BTA. Some preliminary attempts to obtain a more stable and conductive derivative using various complexing ligands for the K^+ ion (such as the crown ethers and cryptates) have been made; however, thus far the desired conductive materials have not been forthcoming. These have included efforts to prepare a mixed valence derivative by co-crystallizing the BTA $^-$ salts with neutral BTA. Work along these lines has been suspended for the present.

Attempts to prepare binuclear complexes using BTA as a bridging tetridentate ligand have centered on the reaction: $2 \text{Ru(bipy)}_2\text{Cl}_2 + \text{BTA} \rightarrow [\text{Ru(bipy)}_2]_2\text{BTA Cl}_2$, which has been studied in both ethanol and acetonitrile solution. In the former case, the preparation of a Ru(bipy)_2 -BTA derivative was evidenced, however it has not been successfully purified and characterized as yet. With acetonitrile the corresponding $\text{Ru(bipy)}(\text{CH CN})^{2+}$ complex was obtained with no indication of a BTA derivative², suggesting a rather weak coordination ability for this species. These efforts to obtain binuclear BTA complexes will be continued using various other metal complexes in addition to the Ru(bipy)^{2+} species.²

C. Other Work

Other work related to the contract effort includes n-efforts to prepare mixed valence crystals of the $\text{NiS}_4\text{C}_4\text{H}_4^{n-}$ complex using large counter ions to promote stacking of the $\text{NiS}_4\text{C}_4\text{H}_4^{n-}$ units, the attempted synthesis of a graphite inclusion compound of $\text{NiS}_4\text{C}_4(\text{CF}_3)_4$, and some studies of benzo-b-quinolizinium (BBQ $^+$) salts of TCNQ. These efforts, which were not successful in producing new conductive materials, are described in detail in our various annual reports (see bibliography).

III. CRYSTALLOGRAPHIC STUDIES

Molecular Displacements in the Spin-Dimerized State of TTF·CuS₄C₄(CF₃)₄ at 4.2K (with D.E. Moncton - Bell Laboratories)

In view of the importance of the spin-Peierls effect for understanding the nature of one-dimensional conductors, it is desirable to know the exact molecular displacements in the spin-dimerized state. Toward that end, we have engaged in a study of the structure of TTF·CuS₄C₄(CF₃)₄ below

the magnetic transition temperature of 12K. Previously x-ray scattering experiments had defined the unit cell and the probably direction of the spin-dimerization axis, but the exact positions of atoms and molecular displacements, requiring measurements of integrated intensities for a large number of reflections, could not be specified. During the past year, integrated intensities for two zones have been obtained and these data have yielded the desired information as to molecular displacements.

The reflections that are characteristic of the spin-dimerized state are very weak (about 1/2% on the average of the main reflections) and a high intensity x-ray source is necessary for their quantitative measurement. Accordingly, the intensity data were obtained with the 50KW rotating anode source at Bell Laboratories, which provides an x-ray flux at least two orders of magnitude greater than that from conventional sources. Despite this advantage it still was not possible to collect all the intensity data that would be needed for a complete structure determination. It was deemed sufficient to use two zones of reflections (161 total) in conjunction with a very plausible simplifying assumption.

It was assumed that the internal geometry of the two molecules remained fixed, as it essentially is at all temperatures from 200 to 300K (except for rotation of CF_3 groups, which ceases below 240K). It was then possible to describe the structure with at most 12 structural parameters rather than the 112 parameters needed for a detailed description of individual atom locations. A program allowing groups of atoms to be maintained rigidly was procured from J. Ibers and modified appropriately for the problem at hand.

An interesting and unforeseen complication regarding intensities from the low-temperature phase was that they were observed to diminish with time. The time for a given intensity to diminish to one-half the initial value was only 31 minutes. It was important, then, not only to collect the data fast but also to apply a correction according to the time at which a measurement was made. It is only the intensities due to the dimerized state that undergo the large changes; no significant change is detectable in the main reflections that are not sensitive to molecular displacements. It would be interesting to investigate the nature of the radiation damage but that was not the purpose of our investigation.

The most appropriate zone for investigating the molecular motions is $(\text{hol})_p$ which can ascertain the motions relative to the soft-mode axis c_p , as well as the other

important directions a_p , and $a_p + c_p$ or c_f . The most significant information was in fact obtained from (hol)_p reflections. The largest effect was a translation of 0.037 \AA of TTF molecules along c_p , the indicated soft-mode direction, i.e. the molecules are paired in this direction with 0.074 \AA shortening between the members of a pair and 0.074 lengthening between paired molecules. The nature of the displacement is indicated in Figure 6. Also, there is a displacement of BDT molecules by only 0.0077 \AA along the diagonal of the primitive cell. Only the centers of mass of BDT molecules are indicated in Figure 6.

The measure of agreement between observed and calculated structure factors is given in Table II. The reflections with even indices are those not sensitive to the molecular displacements and are essentially the same at temperatures slightly above the transition temperature of 12K. The reflections with h and l odd are those that arise below 12K. It appears the agreement is quite satisfactory, considering the assumptions and approximations that have been made.

This investigation establishes then that the spin-dimerization axis is indeed the special direction along which the TTF molecules have the shortest separation, i.e. the direction for a "soft-mode". The smaller displacement of BDT molecules would appear to be a secondary effect resulting from the displacement of TTF molecules. The extent of the molecular translation (.037 \AA for TTF) is in accord with estimates based on the theoretical treatment of the spin-Peierls effect.

This work is completed now and a manuscript is being prepared for publication. The results have been communicated at the Eleventh International Congress of Crystallography, Warsaw, Poland, 3-12 August, 1978.

(TTF)₂(NiS₄C₄H₄)₃

This compound is special among the family of compounds formed by combining TTF with different types of BDT molecules. Its stoichiometry is unusual, there is no charge transfer and it appears to be a solid solution of the two neutral molecules, a circumstance apparently not previously encountered with molecular crystals of this kind.

Its structure is illustrated in Figure 7 in projection on the (001) plane. The cell is monoclinic (space group P2₁/m with the dimensions $a = 11.56\text{\AA}$, $b = 5.22\text{\AA}$, $c = 6.62\text{\AA}$, $\beta = 93.1^\circ$ and contains two sites for molecules. Each of these sites accommodates either a TTF or a NiS₄C₄H₄ molecule in a proportion corresponding to the stoichiometry. The

remarkably close similarity of the two molecules can be seen from the fact that the S and outer C positions are in virtual superposition for both of them and the main difference is the replacement of a C=C pair in TTF by a nickel atom in $\text{NiS}_4\text{C}_4\text{H}_4$. A refinement of the structure with 445 independent reflections has been made with an R factor of 0.081 (F^2 basis), allowing atom location to within 0.01 \AA .

There is not complete disorder, however, as evidenced by additional weak reflections that appear to be incommensurate with the cell given above. A subtle composition variation in one direction is implied leading to a complex scheme of ordering. The exact nature of the ordered structure is being investigated at present and the results will be published along with the structure of the disordered phase. It is planned to make a presentation of the results of our structural studies at the next meeting of the American Crystallographic Association, Hawaii, March 25-29, 1979.

TTT_{1.2}NiS₄C₄H₄

This highly conducting charge-transfer compound is unique in several respects and the structure studies have been of prime importance in understanding its unusual character and peculiar properties. Although from elemental analysis a simple 1 to 1 stoichiometry could be inferred, the structure clearly defined it to be 1.2 to 1. This finding as well as the molecular arrangement deduced from the structure determination allowed a proper interpretation of the magnetic behavior and the nature of the charge transfer.

An interesting feature of the structure is that separate orthorhombic sub-cells are formed by the two molecules. The unit cell for $\text{NiS}_4\text{C}_4\text{H}_4$ molecules has the dimensions $a = 12.73\text{\AA}$, $b = 22.13\text{\AA}$, $c = 8.73\text{\AA}$ with 4 molecules per cell. The $\text{NiS}_4\text{C}_4\text{H}_4$ molecules occur in planes parallel to (010) and are well separated from one another. The sub-cell for the TTT molecules is related to this cell in that $a_{\text{TTT}} = 2a$ and $b_{\text{TTT}} = 2b$ but the c dimensions are quite different: $c_{\text{TTT}} = 3.63\text{\AA}$. The TTT molecules are uniformly stacked in an eclipsed manner along c with the intermolecular separation of 3.63\AA . The consequence is that within a given volume there are 1.2 TTT molecules to one of $\text{NiS}_4\text{C}_4\text{H}_4$, clearly defining the stoichiometry to be 1.2 to 1. Furthermore, the ratio $c/c = \frac{8.73}{3.63} = 2.40 = \frac{12}{5}$ indicates that matching of the two sub-cells occurs for 5 cells of $\text{NiS}_4\text{C}_4\text{H}_4$ and 12 cells of TTT. The structure suggests also a partial filling of a metallic band to the extent of $\frac{7}{12}$.

The structure is illustrated in Figure 8 in projection on the (001) plane in terms of the smaller cell appropriate to $\text{NiS}_4\text{C}_4\text{H}_4$. Figures 9 and 10 give views of the structure for slices parallel to (010), showing both the orientation of $\text{NiS}_4\text{C}_4\text{H}_4$ molecules and the displacement of respective (001) planes normal to c and c' .

The interesting feature of the matching of 12 cells of TTT to 5 cells of $\text{NiS}_4\text{C}_4\text{H}_4$ with the resulting periodicity of 43.6\AA is that this is precisely the periodicity to be expected from a Peierls distortion. The implication is that the TTT molecules are not situated at exactly $\frac{1}{12}$ of the large period but that there probably is a modulation of the z parameter. It would be very interesting to ascertain the individual distortions in the TTT molecular stack, for which there should occur weak satellite reflections. We have searched for such parasitic reflections both with film methods and with a diffractometer but with no success. It should be noted that the crystals for this work were considerably smaller than ideal and efforts to grow larger good crystals have not been successful. It is quite possible that the molecular displacements are very small indeed and the special diffraction effects would be observable only from larger crystals and more intense x-ray sources (cf. the experience with the spin-Peierls effect for $\text{TTF}\cdot\text{CuS}_4\text{C}_4(\text{CF}_3)_4$).

Of necessity, then, we are able to report for publication only on the gross structure as described here and do not plan to do any further search for satellite reflections.

BBQ(TCNQ)₂

Structure studies of this compound were made when it was ascertained that it was a highly conductive one-dimensional system. The final analysis showed the structure to be remarkably similar to that of a compound containing an isomer of BBQ, namely acridinium, ARDH. Once it was learned that conductivity studies had already been made in the USSR, it did not seem worthwhile to pursue the structure studies with small hope of uncovering any subtle difference between the BBQ compound and the acridinium compound. A more detailed account of the work is given in Semiannual Status Report No. 3, SRD-78-061.

SECTION 3

OTHER ACTIVITIES

During the period of this contract Dr. John Kasper has served on a Panel appointed by the National Academy of Sciences to report on "Low Energy Neutron Research in the United States: A Study of the Facilities and Scientific Opportunities". In addition he served as Chairman of the Sub-Panel on "Structures". A report has been completed and published by the National Academy of Sciences (1977). Also Dr. Kasper has served as a member of the Crystallographic Committee of an ERDA workshop to evaluate the status and opportunities of various methods and techniques for the study of the structure of matter. The workshop was held at the Oak Ridge National Laboratory in April, 1977. For the period September 1975 to April 1976 Dr. Kasper was on leave as a Visiting Professor at the University of Bordeaux where he carried out structural studies on new borides.

Dr. Interrante has served as Chairman of the Symposium "Recent Advances in Inorganic and Organometallic Chemistry", at the April, 1976 Centennial Meeting of the American Chemical Society in New York and of the 1976 Gordon Research Conference on Inorganic Chemistry which focused on the topic "Cooperative Effects in Inorganic Chemistry". For a one-week period in April 1977 he served as a guest lecturer in the course "Perspectives in Industrial Research" at the University of California at Riverside. For the past two years he has participated in the annual review of the Materials Science Program of the Ames Laboratory, DOE in Ames, Iowa as an external reviewer. In September, 1977 Dr. Interrante visited France as a guest of the French CNRS to present lectures at a Summer School on the topic "Transition Metal Complexes with Unusual Solid State Properties" and to visit various laboratories where work on 1-D materials was in progress.

Dr. Interrante was elected to the post of Secretary-Treasurer of the Inorganic Division of the ACS in 1977 and has served in this capacity since January 1978. In September 1978 he attended a NATO Advanced Research Institute on "Molecular Metals" in Les Arcs, France and served as Recording Secretary for the Study Group on "Extensions and Reevaluations of Existing Systems" at this Institute. The purpose of this meeting was "to bring together experts to make critical assessments of the existing knowledge in the field and to try to reach concensus in identifying potential in the field and indicating useful research directions for the benefit of the scientific community at large". He has also been asked to participate in a NAS sponsored workshop on "Synthesis and Characterization of Advanced Materials" as a member of the panel on "The Interdependence of Synthesis and Characterization". This workshop is to be held at the NAS facility in Washington, DC on December 13-14, 1978.

SECTION 4

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10. "Molecular Design of Solid State Systems. Organic-Metal Complex π-Donor-Acceptor Compounds". L.V. Interrante, J.W. Bray, H.R. Hart, Jr., J.S. Kasper, P.A. Piacente and G.D. Watkins, Analys of the N.Y. Acad. of Sciences, 313, 407 (1978).
11. "Thermal and Magnetic Study of Exchange in the Quasi-1-D Molecular Compound, TTF·PtS₄C₄(CF₃)₄", J.C. Bonner, T.S. Wei, H.R. Hart, Jr., L.V. Interrante, I.S. Jacobs, J.S. Kasper, G.D. Watkins and H.W.J. Blöte, J. Appl. Phys., 49, 1321 (1978).
12. "The Spin-Peierls Transition and Other Aspects of the Magnetic Behavior of the Compounds, TTF·MS₄C₄(CF₃)₄ (M = Pt, Cu, Au)", L.V. Interrante, J.W. Bray, H.R. Hart, Jr., I.S. Jacobs, J.S. Kasper and P.A. Piacente, Proceedings of the International Conference on Quasi One-Dimensional Conductors, Lecture Notes in Physics (Springer-Verlag Publ), in press.

TALKS GIVEN

L.V. Interrante

1. Transition Metal Chain Compounds, invited paper, Symposium on Delocalized Electrons in Solids, Brown University, August 21, 1975.
2. The Study of One-Dimensional Mixed Valence State Systems at Ultra-high Pressures, invited paper, Symposium on Mixed Valence State Systems, American Chemical Society Meeting, Chicago, Illinois, August 25, 1975.
3. Molecular Systems with Unusual Solid State Properties. II-Donor-Acceptor Compounds of Tetrathiafulvalene with Planar Metal Complexes, Department Colloquium, University of West Virginia, October 1, 1975.
4. Molecular Systems with Unusual Solid State Properties. II-Donor-Acceptor Compounds of Tetrathiafulvalene with Planar Metal Complexes, Department Colloquium, California Institute of Technology, October 27, 1975.
5. Donor-Acceptor Derivatives of Tetrathiafulvalene with Bis-Dithiolene Metal Complexes, invited paper, Pacific Coast Conference on Chemistry and Spectroscopy, October 29, 1975.
6. Molecular Systems with Unusual Solid State Properties. II-Donor-Acceptor Compounds of Tetrathiafulvalene with Planar Metal Complexes. Department Colloquium, University of California at Santa Barbara, November 6, 1975.
7. Evidence for One-Dimensional Solid State Interactions in Some Organic-Metal Complex Systems, Department Colloquium, Howard University, November 20, 1975.
8. Molecular Solids with Unusual Magnetic and Electrical Complexes, invited paper, Mid-Atlantic Regional American Chemical Society Meeting, Philadelphia, Pennsylvania, February 23, 1976.
- 9-10. Organic-Metal Complex Systems with Unusual Solid State Properties. I. The TTF·MS₄C₄(CF₃)₄ Derivatives. A New Class of Low-Dimensional Magnetic Systems, and II. The TTF and TTT Derivatives of NiS₄C₄H₄. Compounds with Moderate High Conductivities, Poster Display presentations, Gordon Conference on Inorganic Chemistry, New Hampton, N.H., August 2-6, 1976.

11. Transition Metal Chain Compounds, invited paper, Symposium on Conducting Materials, 7th ACS Northeast Regional Meeting, State University of New York at Albany, August 11, 1976.
12. Synthesis and Solid State Properties of π-Donor-Acceptor Compounds Based on Bis-dithiolene Metal Complex Acceptors, NATO-ASI on "Chemistry and Physics of One-Dimensional Metals", Bolzano, Italy, August 26, 1976.
- 13-19. Molecular Design of Solid State Systems. Synthesis and Solid State Properties of Organic-Metal Complex π-Donor-Acceptor Compounds, invited presentation at the Inorganic Discussion Weekend, Ottawa, Canada, Oct. 1, 1976; Chemistry Department Seminars at M.I.T., Nov. 3, 1976; Brooklyn College, Nov. 17, 1976; Univ. of California at Berkeley, Dec. 1, 1976; Univ. of South Carolina, March 11, 1977; Univ. of California at Riverside, April 28, 1977; and the Materials Science Colloquium, M.I.T., Feb. 25, 1977.
20. Molecular Design of Solid State Systems. Organic-Metal Complex π-Donor-Acceptor Compounds, invited paper, Symposium on "Synthesis and Properties of Low-Dimensional Materials", sponsored by the N.Y. Academy of Science, New York, N.Y., June 1977.
21. Spin-Lattice Dimerization in Quasi-One-Dimensional Spin Systems, invited paper, ACS Symposium on "Chemical Physics of One-Dimensional Organic Conductors", Chicago, Ill., August 30, 1977.
- 22, 23. Metal Complexes with Unusual Properties in the Solid State, invited lectures at a CNRS sponsored summer school on Co-ordination Chemistry, Solignac, France, September 11-13, 1977.
- 24-26. Molecular Solids with Unusual Properties Obtained from the Interaction of Organic Molecules with Transition Metal Complexes, Department Colloquium at the Laboratoire de Chimie de Coordination, Toulouse, France, Sept. 15, 1977; the University of Paris-Sud, Orsay, France, Sept. 21, 1977; and the University of Bern, Bern, Switzerland, Sept. 23, 1977.
- 27-28. Molecular Solids with Unusual Properties Obtained from the Interaction of Organic Molecules with Transition Metal Complexes, University of Delaware, Department Colloquium, October 21, 1977; Bell Laboratory, Inorganic Chemistry Colloquium Series, October 28, 1977.

29. The Spin-Peierls Transition and Other Aspects of the Magnetic Behavior of the Compounds TTF·MS₄C₄(CF₃)₄ (M = Pt, Cu, Au), International Conference on Quasi One-Dimensional Conductors, Dubrovnik, Yugoslavia, September 6, 1978.
30. Molecular Solids with Unusual Solid State Properties, Washington State University, November 9, 1978.

J. S. Kasper

1. The Crystal Structure of an Unusual Donor-Acceptor Compound (TTF)₂NiS₄C₄H₄, American Crystallographic Association (ACA) Meeting, March 9-13, 1975, University of Virginia.
2. Structures and Properties of One-Dimensional Systems, Department Colloquium, Laboratoire de Chimie du Solide de CNRS, University of Bordeaux, France, December 1, 1975.
3. Structure of the One-Dimensional Conductor (TTF)_{1.2}NiS₄C₄H₄, ACA Meeting, Asilomar, California, February 21-25, 1977.
4. Molecular Displacements in the Spin-Dimerized State of TTF·CuS₄C₄(CF₃)₄ at 4.2K, 11th International Congress of Crystallography, Warsaw, Poland, August 10, 1978.

Table I
NEW π -D·A COMPOUNDS PREPARED USING BIS-DITHIOLENE
METAL COMPLEXES^a

$A \backslash D$	TTF		TTT		BMBD	OMBD
<u>$MS_4C_4X_4$</u>	$1:1^b$ $<10^{-9}c$		-		-	-
X = CF ₃ M = Ni, Pt, Cu, Au	3:2 1×10^{-4}	1:2 3×10^{-3}	1.2:1 14	? 3×10^{-2}	? 2×10^{-8}	? 1×10^{-7}
X = H M = Ni	N.R. ^d	? Pd 0.6, Pt 0.2		-		-
X = CH ₃ M = Ni	N.R.	? 3×10^{-5}		-	-	-
X = C ₆ H ₅ M = Ni	N.R.	~1:1 9×10^{-2}		-	-	-
<u>$M(S_2C_6XY_3)_2$</u>	$\sim 1:1$ 5×10^{-9}		$\sim 1:1$ 1×10^{-3}		N.R.	-
X = CH ₃ , Y = H M = Cu	$\sim 1:1$ 1×10^{-6}	1:1 4×10^{-2}		N.R.	-	-
X = CH ₃ , Y = H M = Co	$\sim 1:1$ 7×10^{-8}	1:1 8×10^{-2}		$\sim 1:1$ 3×10^{-6}	-	-
X = Y = H M = Ni	? 3×10^{-2}	~1:1 8×10^{-2}		1:1 7×10^{-3}	? 6×10^{-6}	-
X = Y = H M = Cu	$\sim 1:1$ 6×10^{-6}	1:1 3×10^{-2}		N.R.	-	-
X = Y = H M = Co	$\sim 1:1$ 1×10^{-7}	1:1 6×10^{-2}		N.R.	-	-
X = Y = CH ₃ M = Ni	? 8×10^{-5}	$\sim 1:1$ 3×10^{-5}		-	? 4×10^{-5}	-
X = Y = F M = Ni	1:1 1×10^{-7}	? 1×10^{-7}		-	? 2×10^{-7}	-

a) prepared either by direct reaction of the neutral components or by metathesis; structures of D and A molecules are given in Figure 4.

b) the stoichiometry of the compound as A:D, where determined by elemental analysis.

c) the conductivity at 25°C, measured using a polycrystalline sample.

d) indicates no new D·A compound formed as evidenced by x-ray powder diffraction patterns and/or elemental analyses of products.

e) indicates composition uncertain, due to either poor analytical results or lack of information.

Table 2
Observed and Calculated Structure Factors
Crystal A

<u>hkl</u>	<u>F_{obs.}</u>	<u>F_{calc.}</u>	<u>hkl</u>	<u>F_{obs.}</u>	<u>F_{calc.}</u>
101	0.4	0.2	200	45	50
301	1.5	1.7	400	78	70
501	1.3	2.5	600	19	25
701	1.8	2.1	800	144	145
901	4.6	5.6	10.0.0	14	28
11.0.1	8.2	9.5	12.0.0	51	63
13.0.1	6.2	6.8	002	44	45
103	1.9	1.9	202	24	29
303	2.2	2.2	402	47	47
503	7.5	7.0	602	92	93
703	0.9	0.5	802	35	30
903	7.2	7.4	10.0.2	131	148
11.0.3	5.4	4.6	12.0.2	71	78
13.0.3	2.6	3.9	004	36	41
105	2.4	2.7	204	20	8
305	1.8	1.9	404	105	102
505	4.5	5.2	604	14	9
705	5.5	5.9	10.0.4	26	34
905	2.5	3.6	12.0.4	23	25
11.0.5	3.3	2.7	006	79	77
107	10.8	9.5	206	97	97
307	2.9	1.9	406	107	102
507	1.1	2.3	606	65	41
707	2.3	2.9	806	31	27
907	2.9	3.4	10.0.6	42	41
109	6.8	7.1	008	154	150
309	18.2	17.0	208	7	3
509	7.1	4.4	408	129	120
709	1.8	1.5	608	21	20
301	1.0	1.5	206	77	66
501	2.0	1.9	806	45	50
701	2.6	1.0	10.0.6	72	77
901	6.8	7.1	808	120	116
11.0.1	1.3	2.2	10.0.8	31	28
103	0.7	0.6	12.0.8	36	29
105	1.5	1.1	14.0.8	59	52
107	1.9	0.5	16.0.8	83	80
307	1.6	1.3	10.0.10	71	72
707	2.6	1.2	12.0.10	14	13
907	5.9	5.6	14.0.10	36	45
11.0.7	4.2	4.5			
13.0.7	3.2	3.1			R = 0.094
15.0.7	4.3	4.9			
17.0.7	4.3	4.3			
109	10.5	10.6			
309	5.7	6.6			
11.0.9	6.1	6.6			
13.0.9	0.4	0.7			
15.0.9	6.2	5.4			
9.0.11	6.6	5.7			
11.0.11	2.2	0.8			
13.0.11	6.4	4.4			
15.0.11	1.6	2.5			
9.0.13	2.6	3.4			
11.0.13	5.0	3.5			
13.0.13	7.6	8.9			

R = 0.176

Section 5

FIGURES

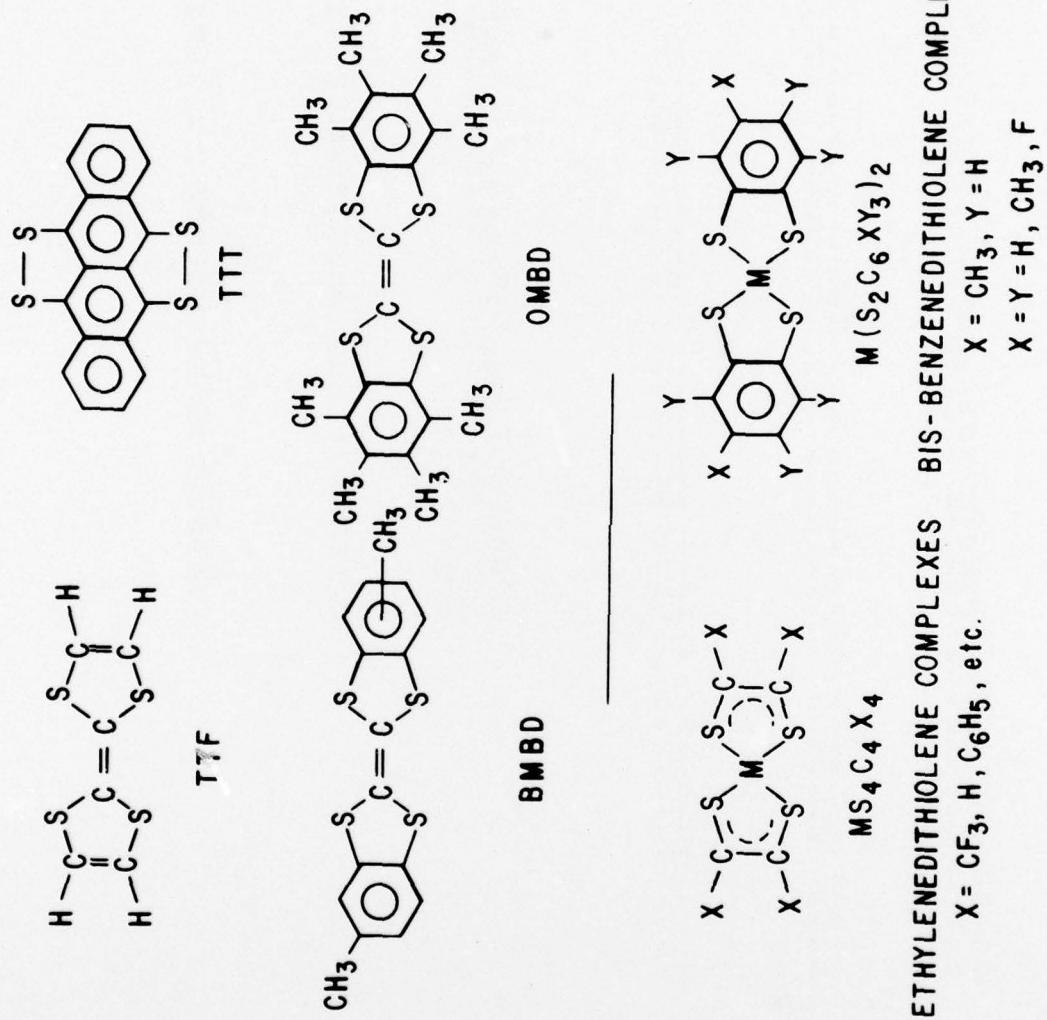


FIGURE 1

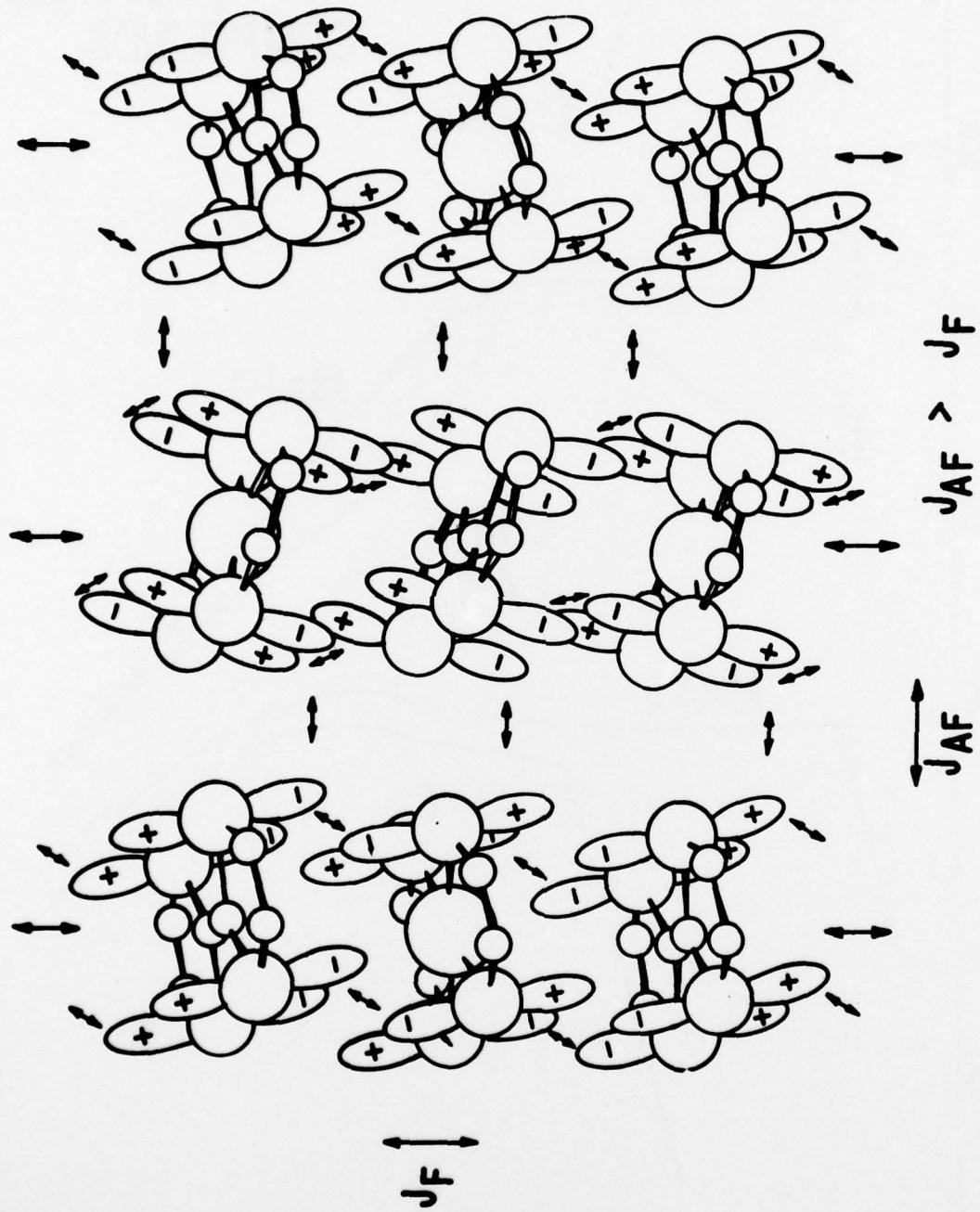


FIGURE 2

Proposed magnetic exchange interactions in the bc plane
of $\text{TTF}^+ \text{NiS}_4\text{C}_4(\text{CF}_3)_4^-$ structure.

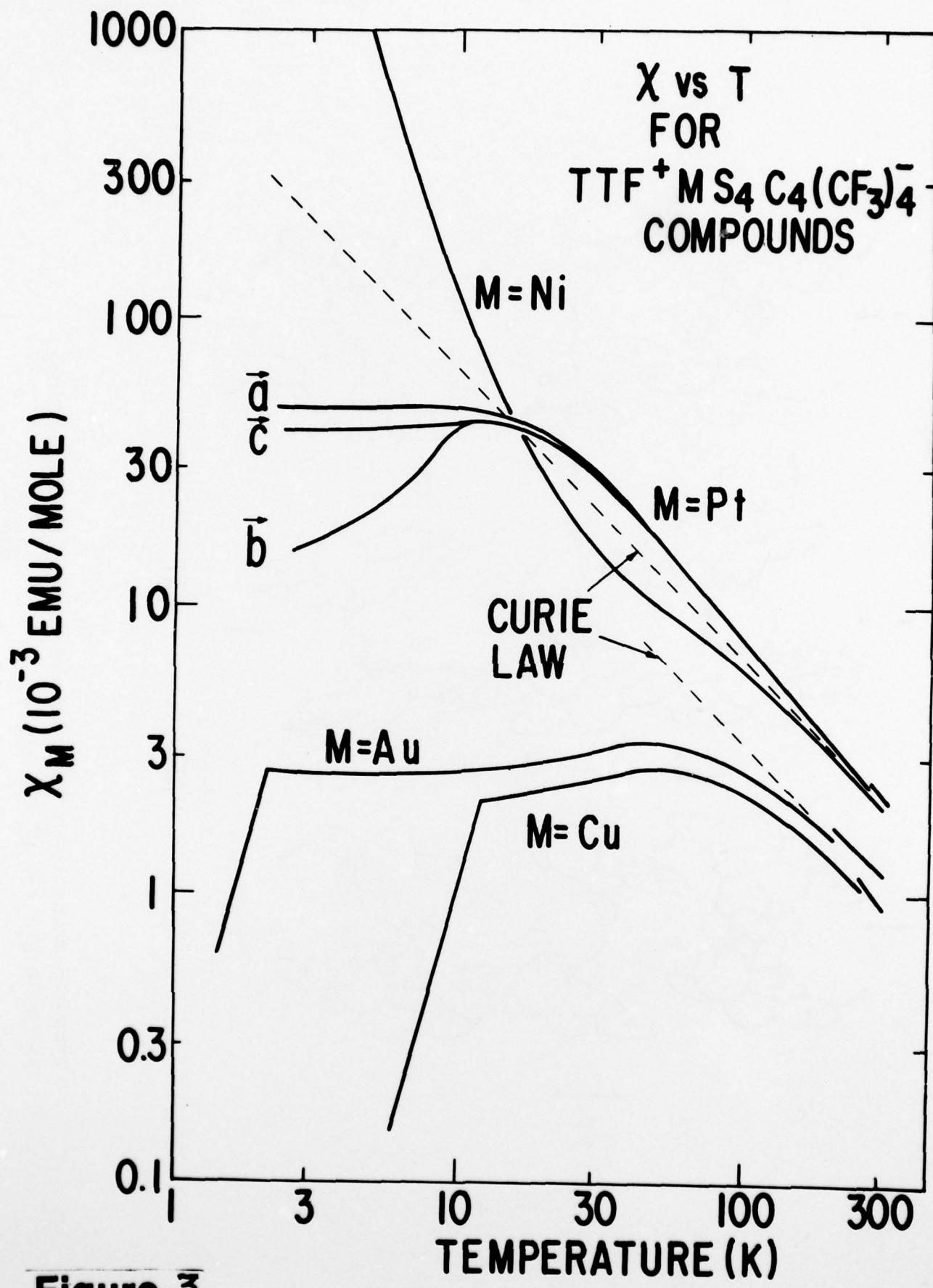


Figure 3

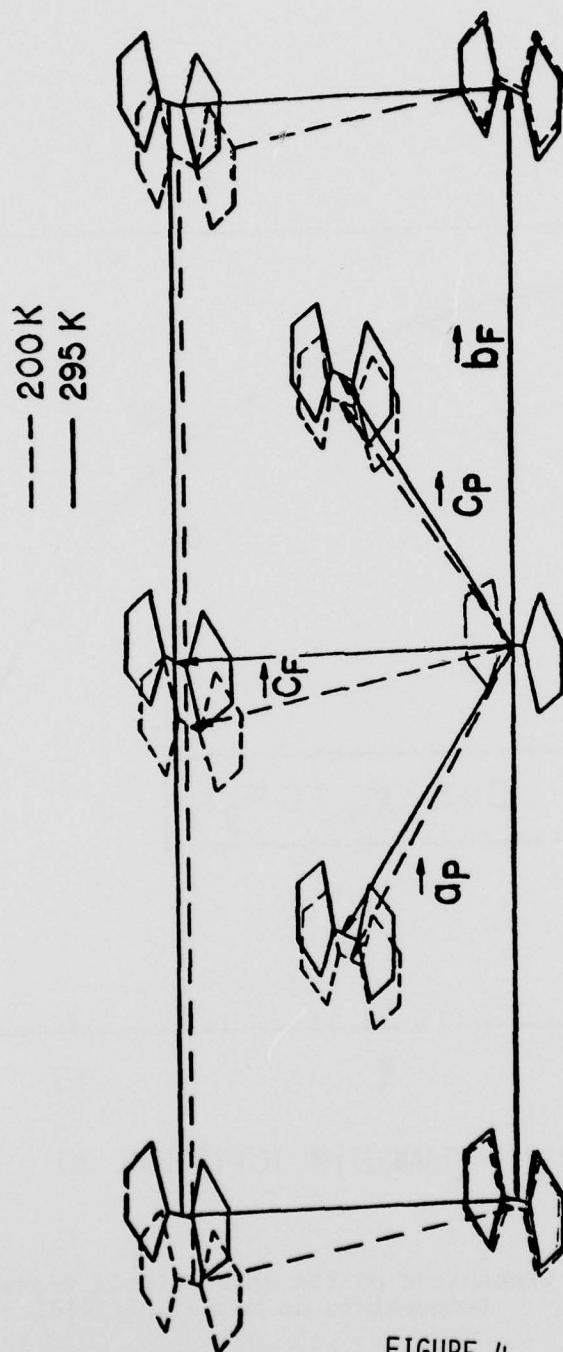
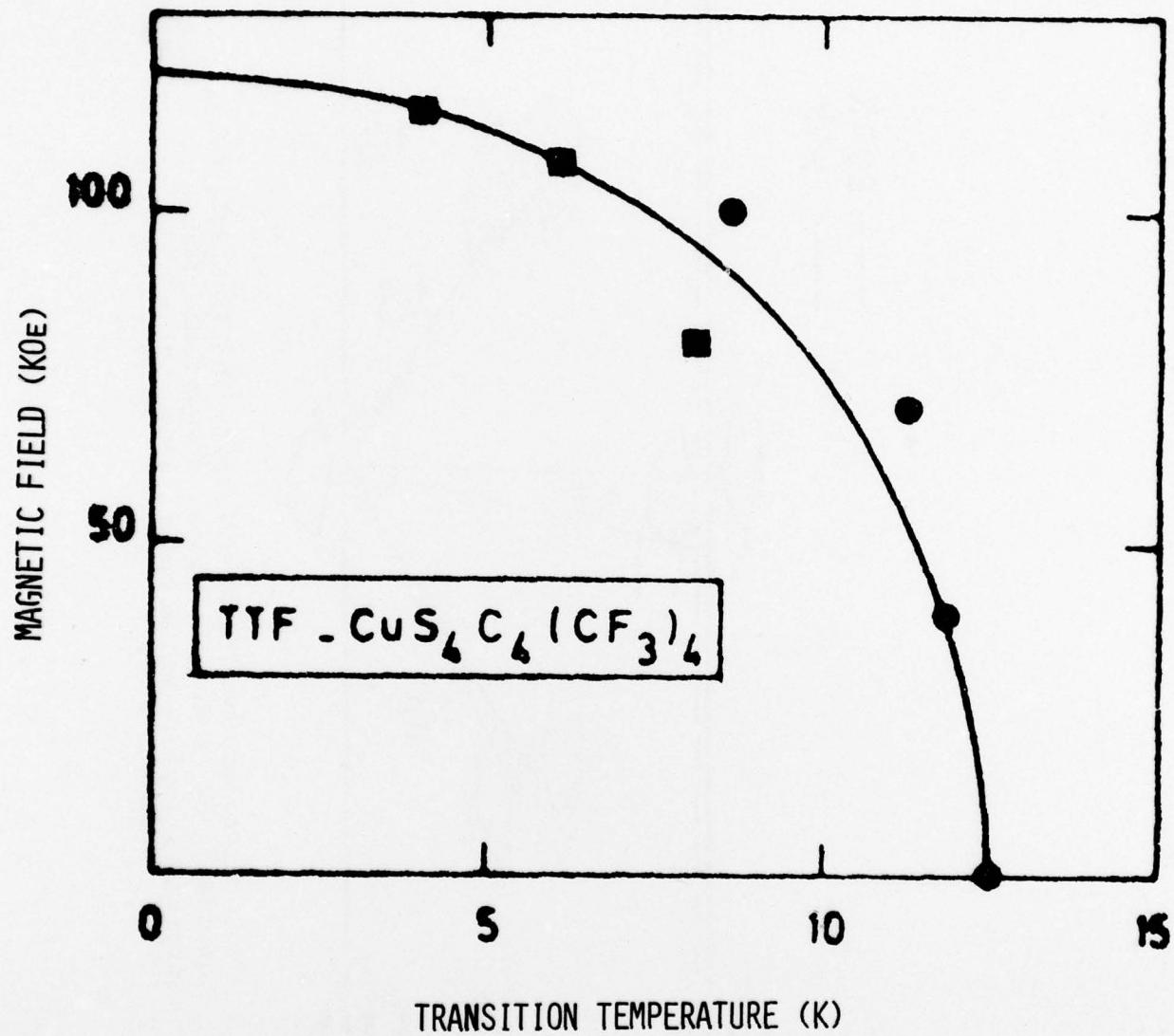


FIGURE 4

A projection of the TTF units in $\text{TTF} \cdot \text{C}_4\text{SuC}_4(\text{CF}_3)_4$ on the $\vec{c}_p - \vec{c}_F$ or $\vec{c}_F - \vec{b}_F$ plane, showing the change in crystal structure which occurs at $T_s \sim 240\text{K}$.



Dependence of the spin-Peierls transition temperature on magnetic field.

FIGURE 5

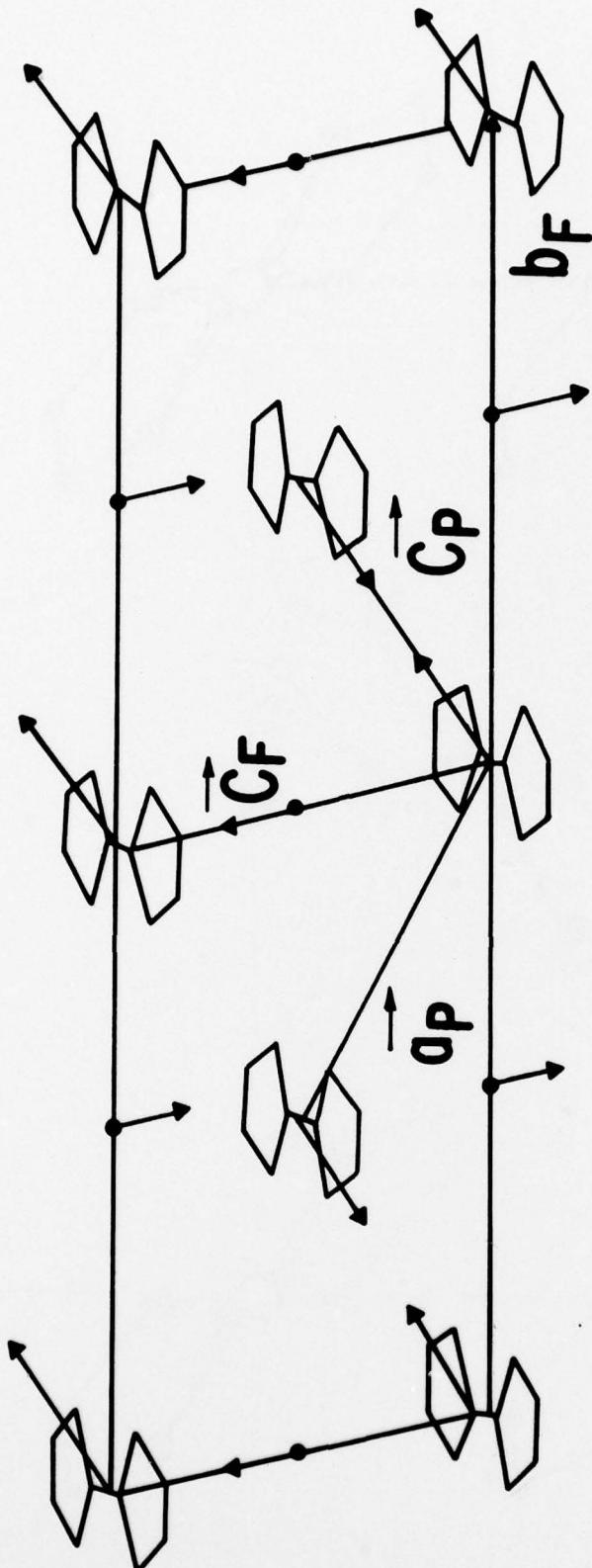


FIGURE 6

Directions of displacements for the TrF^+ and $\text{CuS}_4\text{C}_4(\text{CF}_3)_4^-$ units (only the center of mass of the latter species is shown here, for clarity) below the spin-Peierls transition temperature.

Projection of the $(\text{TTF})_2(\text{NiS}_4\text{C}_4\text{H}_4)_3$ crystal structure on the (001) plane.

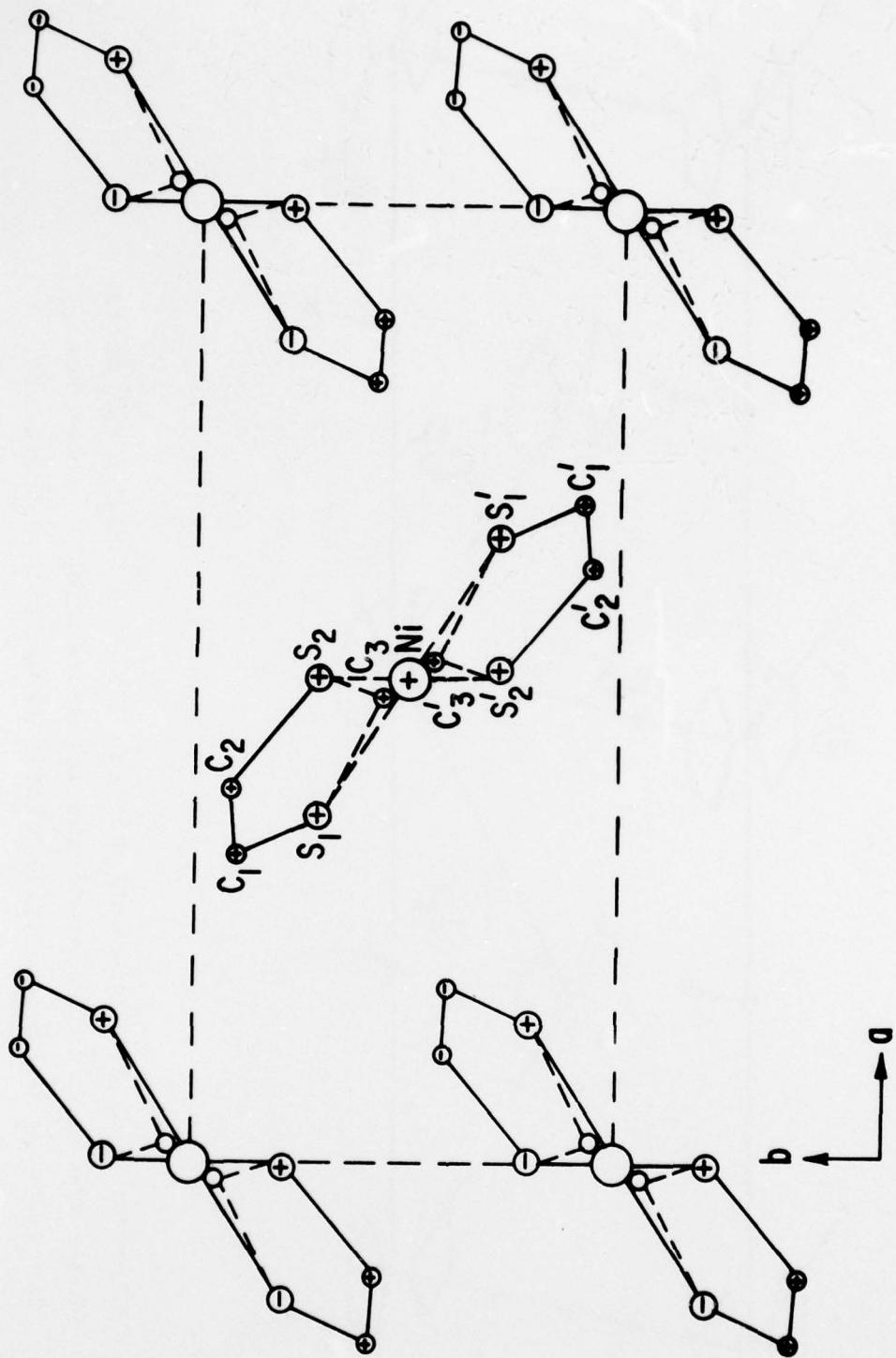


FIGURE 7

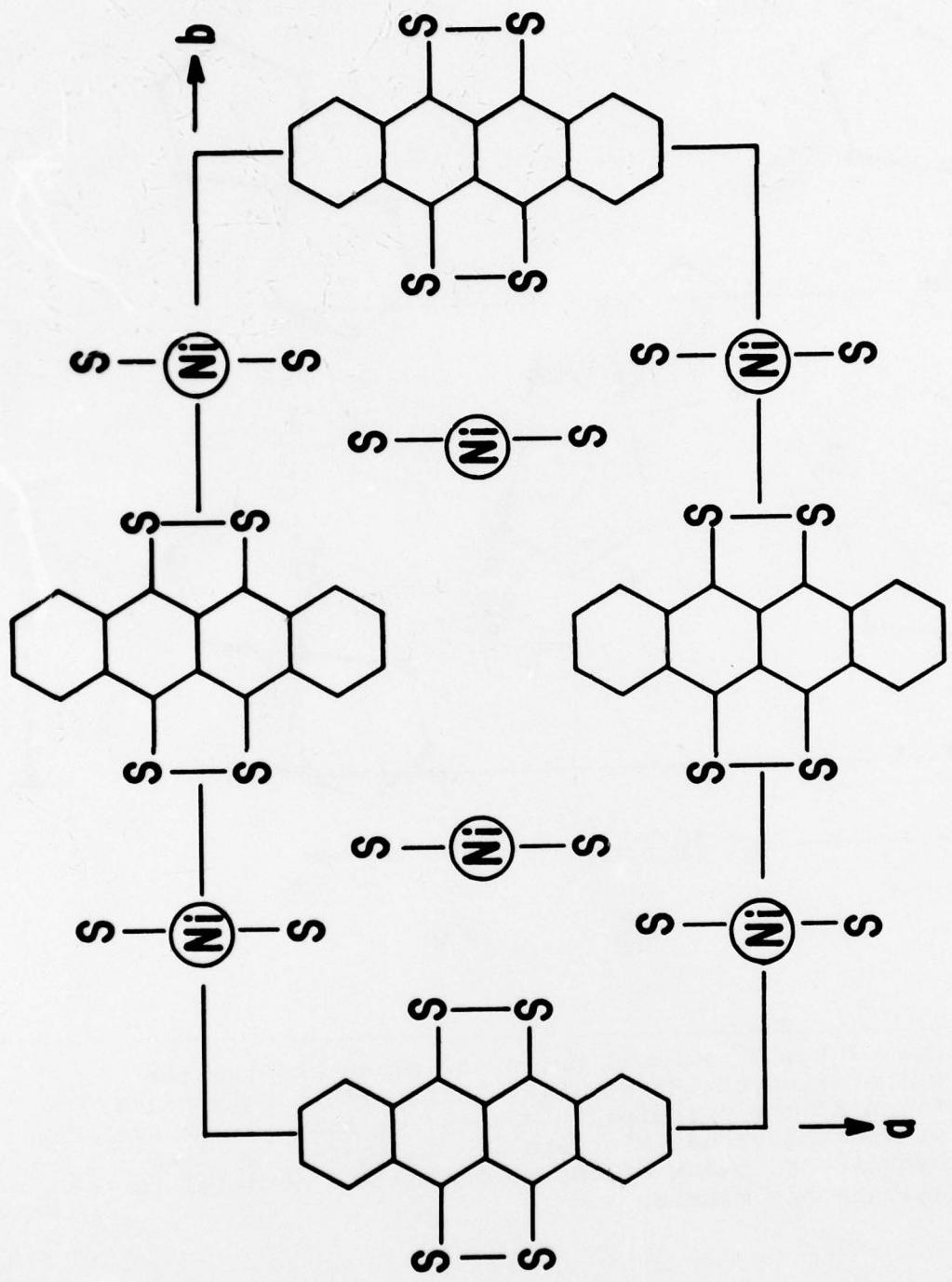
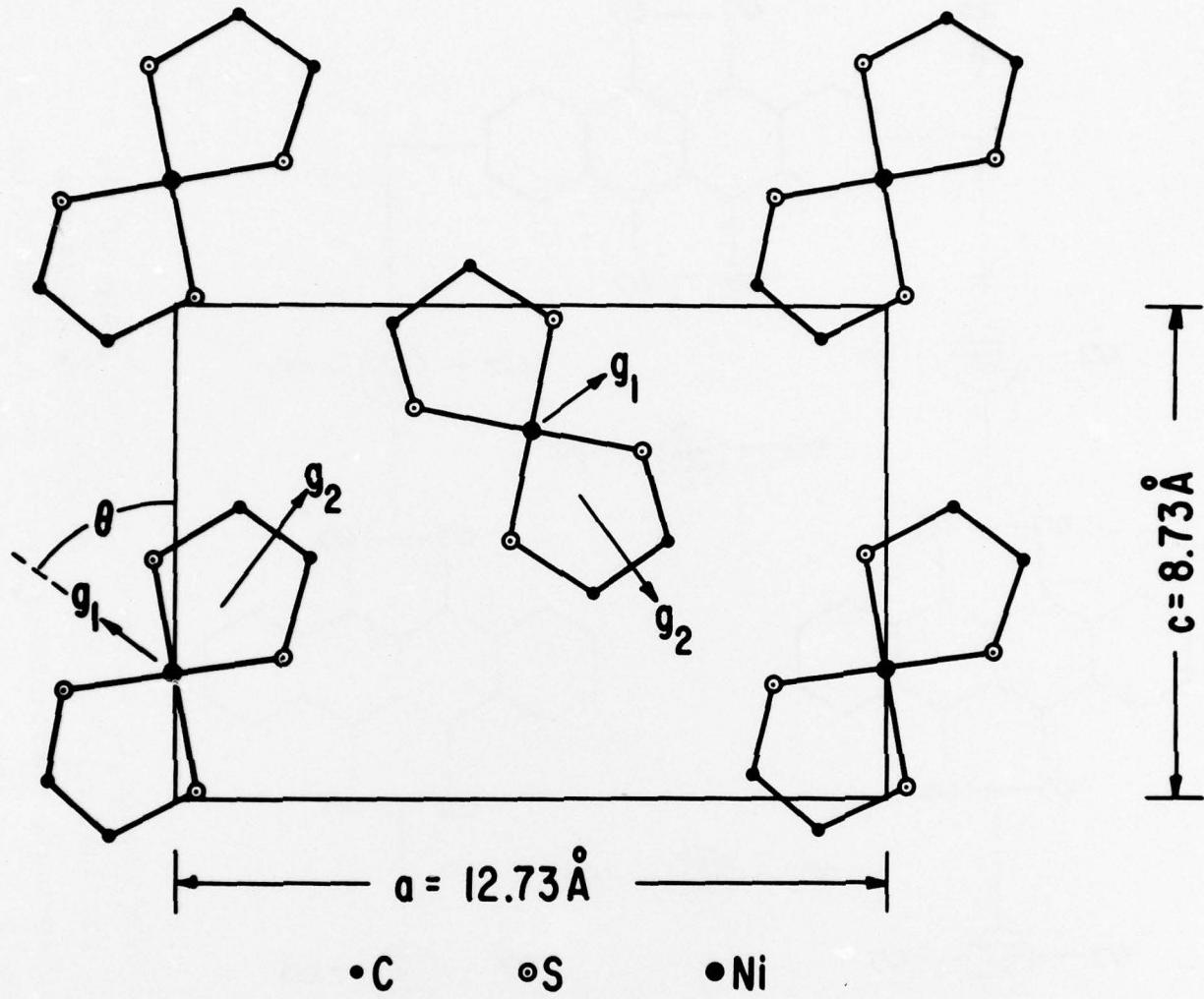


FIGURE 8

A projection of the $\text{TTT}_1 \cdot 2\text{NiS}_4\text{C}_4\text{H}_4$ structure on the ab plane of the $\text{NiS}_4\text{C}_4\text{H}_4$ subcell ($a_N = 12.7\text{\AA}$, $b_N = 22.13\text{\AA}$). Ni indicates positions of the Ni and the approximate positions of two of the S atoms of the $\text{NiS}_4\text{C}_4\text{H}_4$ unit. These S atoms lie, respectively, above and below the Ni in the actual structure.



A projection of the N^- subcell on the ac plane showing the relative orientation of the $NiS_4C_4H_4^-$ units within this plane. The directions of the principal g values, g_1 and g_2 , characteristic of the individual N^- units are indicated; g_3 lies perpendicular to the plane of the molecules and parallel to the crystallographic b axis.

FIGURE 9

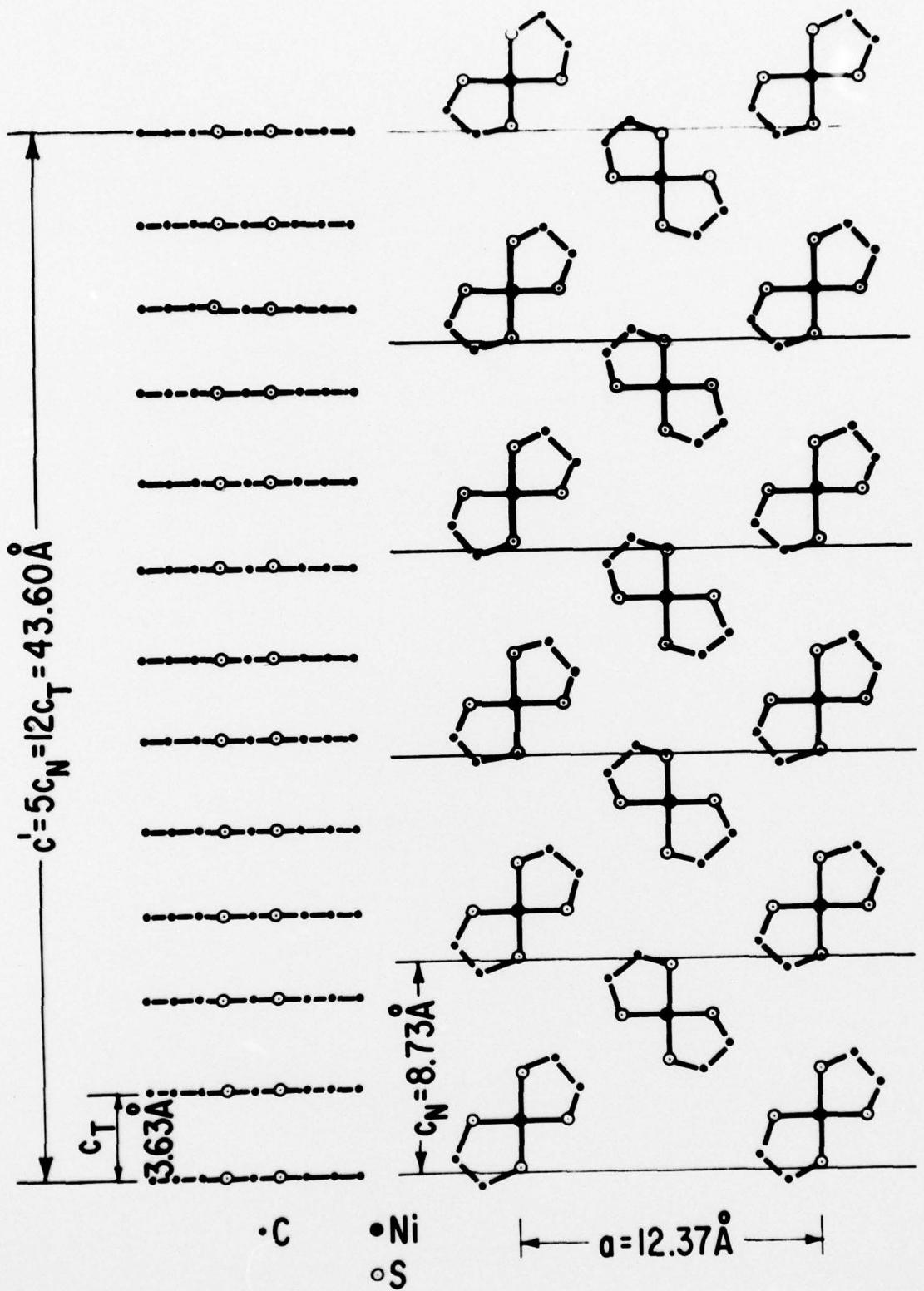


FIGURE 10

A view of the two subcells in the $\text{TTT}_{1.2}\text{NiS}_4\text{C}_4\text{H}_4$ structure normal to the ac plane, showing the coincidence of the $\text{NiS}_4\text{C}_4\text{H}_4$ and TTT subcells at $5c_N = 12c_T$.